



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(54) Title: METHOD FOR CLEANING ITEMS IN PARTICULAR FILTERS, USED DURING FOODSTUFF PRODUCTION</p> <p>(57) Abstract</p> <p>The invention relates to a method for cleaning apparatus used during the production of foodstuffs, in particular the filtration thereof, wherein this apparatus is contacted after use with a cleaning system based on the combination of a cyclic nitroxyl compound and a hypohalite.</p>		

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**METHOD FOR CLEANING ITEMS IN PARTICULAR FILTERS, USED DURING FOODSTUFF PRODUCTION**

The invention relates to the cleaning of apparatus used during the production, processing or treatment of foodstuffs, more in particular the filtering thereof. An important example thereof is the cleaning of apparatus for  
5 brewing beer and more in particular the cleaning of filters, such as membrane filters for filtering residual beer and settled beer. Within the context of this invention the term "production" is used to indicate all treatments carried out on foodstuffs, such as production, treatment, processing and  
10 the like.

During the production of foodstuffs, such as milk (products), fruit juices, beer, soft drinks (such as lemonades), cider, wine, sherry, port, distilled drinks and the like, the problem often occurs that apparatus must be  
15 cleaned after a certain period, because components from the material to be treated are adsorbed or absorbed or precipitate on surfaces of the apparatus, which is undesirable. This may in fact give rise to a disturbance of, on the one hand, the operation of the apparatus and, on the  
20 other hand, the quality of the final product.

The apparatus involved is the apparatus used during the treatment of foodstuffs, more in particular liquids, as indicated above. More in particular, filters are involved, such as membrane filters used for filtering the above  
25 products or semimanufactures therefor.

Examples of such treatments are the production and/or processing of milk and milk products, fruit juices, beer, soft drinks, cider, wine, sherry, port, distilled drinks and the like.

30 In the case of brewing beer the invention relates to, inter alia, the apparatus used during the preparation of malt, the conversion of malt and/or unmalted grain into wort and the further processing of the wort, with or without

addition of extra components, such as hops, by fermentation to beer, as well as all auxiliary apparatus used therewith and coming in contact with main or secondary streams from these processes.

5           An example of the disturbance of the operation of the apparatus is found with the different filters used, e.g. the filters for filtering soft drinks, milk (products), wine, sherry, port, distilled drinks, fruit juices, lemonade, beer, such as settled beer, residual beer, but also the wort/spent  
10 grain separation, hot trub separation and cold trub separation.

          The capacity of filters used in such processes, the flux, decreases in the course of time, which is of course undesirable. This particularly plays a role when use is made  
15 of membrane filters. This capacity decrease can be partly inhibited by rinsing back the filter. After some time, however, this is not sufficient, and it is therefore necessary to clean the filter.

          A further examination has revealed that the  
20 apparatus, and more in particular the filters, become contaminated by a combination of all kinds of compounds, of which polysaccharides, oligosaccharides, proteins,  $\beta$ -glucanes, fats and polyphenols are important components. during the production

25           Conventional cleaning techniques, e.g. based on catalyzed or uncatalyzed oxidation, e.g. with a peroxide/metal (manganese) complex hypochlorite or hypobromite, are not satisfactory, which appears from the fact that the flux cannot be restored to the original value  
30 or close thereto. Nor does the use of detergents or enzymes, such as proteases, carbohydrases, amylases, pullulanases, proteases and lipases, lead to the desired results.

          There is therefore a need for an efficient cleaning system for cleaning apparatus for the production, as defined  
35 above, of liquid foodstuffs, which system is capable of effecting a proper cleaning, which must preferably be done

within a short time (15-120 min) and during which substantially all contaminations are removed.

The invention is based on the surprising insight that it is possible to adequately clean apparatus used during the production of foodstuffs by using a cleaning system on the basis of a combination of a cyclic nitroxyl compound and a hypohalite. This involves removal of contaminations formed during the production of foodstuffs, e.g. precipitated on surfaces of the apparatus or in pores of filters.

The invention therefore relates to a method for cleaning apparatus used during the production of foodstuffs, in which this apparatus is contacted after use with a cleaning system based on the combination of a cyclic nitroxyl compound and a hypohalite in aqueous solution.

Preferably, the cyclic nitroxyl compound is a substituted piperidine, such as 2,2,6,6-tetra-methylpiperidine-*N*-oxyl (TEMPO). This is a commercially available compound (CAS Reg. No. 2564-83-2).

In combination with a hypohalite, preferably a hypobromite, it is possible to obtain a rapid removal of contaminations by using catalytic amounts of TEMPO. The hypobromite, which is preferred, is preferably formed in situ from hypochlorite and alkali metal bromide (most preferably NaBr), so that the reaction system of Fig. 1 is obtained. It is to be noted that preference is given to the use of bromite, since it gives a considerably shorter cleaning time than the chlorite. It is also possible to generate the bromite from other components or to add it as such to the system.

The method according to the invention is most preferably carried out by contacting an aqueous solution of the nitroxyl compound, such as the different nitroxide radicals, e.g. 2,2,6,6-tetra-methylpiperidine-*N*-oxyl (TEMPO), 4-oxo-2,2,6,6-tetra-methylpiperidine-*N*-oxyl (OTEMPO), 4-hydroxy-2,2,6,6-tetra-methylpiperidine-*N*-oxyl (TEMPOL) and other derivatives having the same 2,2,6,6-tetra-

methylnpiperidine-N-oxyl (TEMPO) skeleton, as well as derivatives on the basis of 4,4-dimethyloxazolidine-N-oxyl (DOXYL) and 2,2,5,5-tetra-methylnpyrrolidine-N-oxyl (PROXYL) and the hypohalite in water with the contaminated apparatus.

5           The concentration of the cyclic nitroxyl compound preferably ranges between 1 and 250 mg/l, more in particular between 2 and 25 mg/l. Such concentrations of nitroxyl compound can be properly combined with hypohalite (OBr<sup>-</sup> or OCl<sup>-</sup>) concentrations of at least 0.5 g/l, preferably 0.75 to  
10 10 g/l. In case a system on the basis of hypochlorite, alkali metal bromide and the nitroxyl compound is used, the amount of bromide is significantly lower than the amount of hypochlorite. Since the bromite is regenerated, bromide contents (calculated as Br) of not more than 1 g/l are  
15 sufficient at the above concentrations of the nitroxyl compound.

          In a characteristic method a catalytic amount of TEMPO is used. Only minute amounts of the cyclic nitroxyl compound are necessary, since it functions as a catalyst for  
20 forming the active oxidant, the hypohalite, from hypohalide.

          It is to be noted in this respect that the present system of cyclic nitroxyl compound and hypohalide is known per se, e.g. from WO-A 95/07303. This publication describes the oxidation of carbohydrates with primary hydroxyl groups.  
25 In no manner, however, does it appear therefrom that this system is useful for cleaning apparatus used for the production of foodstuffs, in which the nature of the contaminations is as different as indicated above. This is the more surprising as the conventional cleaning methods on  
30 the basis of hypohalite, e.g. with filters when brewing beer, do not give the desired effect.

          The invention is applicable to all apparatus used during the processing of foodstuffs, and which contacts the main stream and/or the secondary streams of the production.  
35 More in particular, the invention is applicable to the cleaning of filters used for filtering milk, milk products,

soft drinks, cider, wine, sherry, port, fruit juices, distilled drinks, beer, settled beer, residual beer, but also the wort/spent grain separation, hot trub separation and cold trub separation.

5           The contact between cleaning liquid and apparatus may be effected both statically and dynamically, that is to say: the liquid either is stationary or flows through the apparatus. Suitable contact times range between 5 minutes and 2 hours, which times of course also depend on the degree of  
10   contamination, the concentration of the components (more in particular the nitroxyl compound) and the temperature.

          The pH of the cleaning liquid is preferably kept within the alkaline range. In practice, this is a value ranging between 7 and 12. When using only hypochlorite in  
15   combination with the nitroxyl compound, even weakly acid pH values are possible ( $\text{pH} > 6$ ). Since the cleaning is often accompanied with the formation of organic acids, the cleaning can be controlled by means of the amount of caustic required to maintain the adjusted pH. As soon as the caustic  
20   consumption strongly decreases, also after dosing  $\text{HOCl}/\text{HOBr}$ , it can be noticed that the cleaning is terminated. This system has the great advantage that a low concentration of oxidant is sufficient, so that damage to apparatus and parts can be decreased or even completely avoided.

25           After cleaning the apparatus is rinsed and can be used again. It is to be noted that the system according to the invention can be suitably used for each cleaning. It is also possible, however, to alternately clean the apparatus with, on the one hand, a conventional system, e.g. based on  
30   detergents, optionally in combination with peroxides and/or enzymes, and, on the other hand, the system according to the invention. It is also possible to use the system according to the invention as a kind of postcleaning, subsequent to a conventional system.

35           The invention will now be explained by means of some, non-limitative, examples.

**EXAMPLE 1**

By means of a module for filtering settled beer, which was provided with a non-used membrane filter, settled  
5 beer was filtered for some time at a pressure of 0.3 bar. The flux of the beer was determined at a number of times (A).

Then the filter was cleaned for 2 hours with a solution containing 4.5 g/l HOCl, 35 mg/l NaBr and 15 mg/l TEMPO. After the cleaning the test was repeated (B).  
10 This cycle was then carried out one more time (C). In the following table some results are listed.

Table

Time (min)	Flux (l/hour/bar/m <sup>2</sup> )		
	A	B	C
20	1100	1100	1400
30	850	1050	1100



Claims

1. A method for cleaning apparatus, more in particular a filter, used during the production of foodstuffs, wherein said apparatus is contacted after use with a cleaning system based on the combination of a cyclic nitroxyl compound and a hypohalite.
2. A method according to claim 1, wherein apparatus, more in particular a filter used for producing (filtering) milk (products), fruit juices, beer, soft drinks, such as lemonades, cider, wine, sherry, port, distilled drinks and the like, more in particular beer, is cleaned.
3. A method according to claim 1 or 2, wherein a membrane filter is cleaned.
4. A method according to claims 1-3, wherein the cyclic nitroxyl compound is used in a catalytic amount.
5. A method according to claims 1-4, wherein the cyclic nitroxyl compound used is 2,2,6,6-tetra-methylpiperidine-N-oxyl (TEMPO), 4-oxo-2,2,6,6-tetra-methylpiperidine-N-oxyl (OTEMPO), 4-hydroxy-2,2,6,6-tetra-methylpiperidine-N-oxyl (TEMPOL) and other derivatives having the same 2,2,6,6-tetra-methylpiperidine-N-oxyl (TEMPO) skeleton, as well as derivatives on the basis of 4,4-dimethyloxazolidine-N-oxyl (DOXYL) and 2,2,5,5-tetra-methylpyrrolidine-N-oxyl (PROXYL), more in particular 2,2,6,6-tetra-methylpiperidine-N-oxyl (TEMPO).
6. A method according to claims 1-5, wherein the hypohalite used is a hypobromite.
7. A method according to claims 1-6, wherein the hypohalite used is a combination of hypochlorite and an alkali bromide.
8. A method according to claims 1-7, wherein the cleaning system is used as an aqueous solution.

9. A method according to claims 1-8, wherein said cleaning is preceded by a cleaning with another cleaning system.

10. A method for producing one or more foodstuffs, more  
5 in particular beer, in suitable apparatus, wherein said apparatus is regularly cleaned using the method according to any or more of claims 1-9.

11. The use of a cleaning system based on the combination  
of a cyclic nitroxyl compound, preferably in combination with  
10 a hypohalite, for cleaning apparatus used for the production, more in particular the filtering, of foodstuffs.

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D7/54 C11D7/32

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9323 Derwent Publications Ltd., London, GB; Class A97, AN 93-186697 XP002024217 & RO 104 553 A (DERO INTR DETERGENTI) , 25 February 1992 see abstract	1,8
A	DE 36 35 357 A (WELLHOENER VEIT) 21 April 1988 see the whole document	1
A	EP 0 392 395 A (GESSNER & CO GMBH) 17 October 1990 see page 9, line 20 - line 25; claims 1,29	1-3,9



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3635357 A	21-04-88	NONE	
EP 0392395 A	17-10-90	DE 3911697 A	25-10-90
		JP 3117475 A	20-05-91